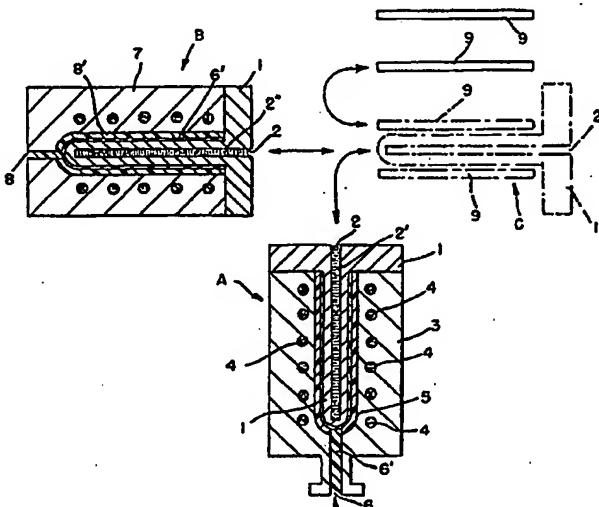


PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : B29C 45/16, 49/22		A1	(11) International Publication Number: WO 95/22451 (43) International Publication Date: 24 August 1995 (24.08.95)
<p>(21) International Application Number: PCT/US95/01646</p> <p>(22) International Filing Date: 9 February 1995 (09.02.95)</p> <p>(30) Priority Data: 08/198,572 18 February 1994 (18.02.94) US</p> <p>(71) Applicant: THE COCO-COLA COMPANY [US/US]; 310 North Avenue, Atlanta, GA 30313 (US).</p> <p>(72) Inventor: PLESTER, George; 1424 Chaussée-de-Mons, B-1070 Brussels (BE).</p> <p>(74) Agents: BIRCH, Anthony, L. et al.; Birch, Stewart, Kolasch & Birch, P.O. Box 747, Falls Church, VA 22040-0747 (US).</p>		<p>(81) Designated States: BR, CA, CN, CZ, FI, HU, JP, MX, NO, PL, RO, RU, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>	
<p>(54) Title: HOLLOW CONTAINERS HAVING A VERY THIN INERT OR IMPERMEABLE INNER SURFACE LAYER BY COATING THE INSIDE SURFACE OF THE PREFORM</p> 			
<p>(57) Abstract</p> <p>A very thin inner layer (6') composed of a polymer chosen for its barrier and/or inertness properties is fabricated within a container preform (8', 14) constructed mainly from another polymer, or a structure of polymers. The inner layer (6') on the preform is produced either by a controlled coating method involving coating of the injection mold core rod (1) prior to injection molding or by a coating applied directly to the preform (14) after injection molding. This enables both inner and main layers to be brought together at a time when the interface between them is molten. A tie layer can be employed, when desirable, to enable the layers to be combined without melting the layer interface.</p>			

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

HOLLOW CONTAINERS HAVING A VERY THIN INERT
OR IMPERMEABLE INNER SURFACE LAYER BY
COATING THE INSIDE SURFACE OF THE PREFORM

BACKGROUND OF THE INVENTION

This invention relates to hollow containers with inert and/or impermeable inner surfaces and, more particularly, to such containers produced by the 5 application of a thin coating either directly to the container preform or to the core rods of the preform injection machine.

Plastic containers have been replacing glass in many applications where easy handling, low weight and 10 non-breakability are needed. To date, polymers have had varying degrees of inertness to the packaged content which differ from the inertness of glass. In the case of plastic food packages, surface inertness helps diminish potential desorption of packaging 15 material components into the food, to prevent flavor absorption, to avoid loss of food constituents through the package walls and to avoid ingress of air or other substances from outside the package.

Refillable plastic packages add a further 20 dimension to inertness requirements because these packages must withstand washing and refilling. Such containers should not absorb contact materials including, inter alia, washing agents and materials stored in the container.

25 Packages for carbonated beverages are pressurized and must withstand considerable mechanical stress in handling. It is therefore difficult for a single material to provide the necessary mechanical stability and the required inertness.

30 Current plastic packages for carbonated beverages consist of either a single material, e.g. polyethylene

- 2 -

terephthalate (PET), or of multi-layer structures where the middle layers normally provide the barrier properties while the outer layers provide the required mechanical strength.

5 Multi-layer containers are produced either by coinjection or coextrusion but these processes restrict choice of materials and cannot provide a very thin inner layer.

10 Therefore, a plastic container with an impermeable, dense, "glass-like" inner surface cannot be produced by conventional methods because these limit the options for the internal surface. Where a plastic, such as high-crystalline PET has good barrier properties but poor transparency, a very thin inner 15 layer is needed so that the transparency of the container as a whole is not impaired. Where a plastic, intended as inner layer, has a different glass transition temperature than the main container material, it cannot be blow-molded unless the inner 20 layer is very thin and can be subjected to individual heat treatment. And, where a barrier plastic has residual monomers or depolymerization by-products, such as acetaldehyde for PET, these can be extracted or deaerated from a very thin layer but not from a 25 thick layer. Accordingly, more polymer options are possible with very thin layer structures.

Recycling is yet another dimension insofar as mass-produced packages are concerned. The reuse of 30 recycled plastic for same purpose, that is to produce new containers ("closed-loop" recycling) is an issue which has attracted much attention, and for PET, this has been achieved to-date by depolymerizing the recycled material in order to free it of all trace 35 contaminants which might otherwise migrate and come in contact with the container content. An impermeable inner layer, which is the purpose of this invention,

would enable recycled material to be reused directly for new containers i.e. without special treatment such as depolymerization, since traces of foreign substances could no longer contact the container's content. This would simplify the "closed-loop" recycling process considerably by obviating the need for depolymerization.

Furthermore, recyclability within established recycling systems, both "open-loop", i.e. recycling for other uses, or "closed-loop", i.e. reuse for same purpose, is necessary for any mass-produced package. In "open-loop" systems, the normal method is to separate, clean and chop up the plastic into small flakes. The flake is then either melted and used for molding other objects, or for fibre production. For this form of recycling, it is important to note that any contaminant to the main plastic, such as a coating, should effectively be present in negligible quantities and, preferably, be solid and insoluble within the molten plastic so that it can be filtered off prior to sensitive applications, such as fibre-production. PET is also recycled in "closed-loop" by depolymerization and it is important that the coating material should be unchanged by this process, be insoluble in the monomers resulting from the process, and be easily separable from these monomers. With a correct choice of material, a thin, inner layer can fulfill these criteria.

Finally, since one option available when using a single very thin layer is to use a highly crystalline version of the same polymer as is used in the main part of the container, e.g. highly crystalline PET in PET containers, the inner layer is virtually the same as the outer and recycling presents no problems.

As a result of these inherent limitations, current technology cannot now produce containers with

- 4 -

a high barrier inert inner layer having a good appearance because it forces compromises which detract from the desired end result which is an improved beverage container.

5

SUMMARY OF THE INVENTION

Accordingly, it is the primary object of this invention to fabricate a very thin inner layer composed of a polymer chosen for its barrier and/or inertness properties within a container constructed 10 mainly from another polymer, or same polymer in a significantly more crystalline state, or a structure of polymers.

This and other objects are fulfilled by a method and apparatus for forming a thin inner polymer layer 15 within the preform, then further reducing the thickness of this layer when the container is subsequently formed by stretch blowing. The inner layer on the preform is produced either by a controlled coating method involving coating of the 20 injection mold core rod prior to injection molding or by a coating applied directly to the reheated surface of the preform after injection molding. This enables both inner and main layers to be brought together at a time when the interface between them is molten. 25 Such fabrication offers resistance to subsequent delamination. Additionally, this enables one to use a conventional tie layer, if necessary, and also enables the layers to be combined, where appropriate, without melting the layer interface. Furthermore, 30 this enables use of an inner layer whose glass transition temperature is different from that of the main material in the preform.

Since a very thin layer of polymer is used, the 35 problems of residual monomers, or other extractables, can be resolved by conventional means, such as by deaeration or extraction which is at present far less

- 5 -

practicable when the material layer used is thicker, or when the material in contact with the food does not present a good barrier to migration from other layers within the container wall structure. Finally, since 5 some barrier materials have poor transparency, the use of a very thin layer enables transparency problems to be avoided or at least reduced. This invention therefore provides greater flexibility in selecting the material for the inner contact layer of a 10 container on the basis of its barrier properties and inertness, thereby avoiding undesirable compromises which are imposed by the current technology.

BRIEF DESCRIPTION OF THE DRAWINGS

15 The present invention will become more fully understood from the detailed description given hereinbelow and the accompanying drawings which are given by way of illustration only, and thus, are not limitative of the present invention and wherein:

20 Figure 1 is a diagrammatic view of a method in accordance with a first embodiment of the present invention;

Figure 2 is a diagrammatic view of an alternative method in accordance with a second embodiment of the present invention;

25 Figure 3 is a cross sectional view of Figure 2 taken along the lines 3-3 thereof;

Figures 4A-4C are cross sectional views illustrative of a third method of the present invention; and

30 Figure 5 is illustrative of the pre-stretch blowing reheating apparatus used in connection with the present invention, whenever differential heating is required for the inner layer.

DETAILED DESCRIPTION OF THE INVENTION

35 Referring now to the drawings and more particularly to Figure 1, shown thereat is a preferred

- 6 -

method in accordance with this invention for providing injection molding core rods with a coating of a molten barrier material as an added function of a conventional injection molding machine.

5 According to Figure 1, a conventional injection molding core rod 1 is first heated internally at A by passing a heating fluid 2' into the channel 2. A core rod receiver 3 has a plurality of channels 4 and an inner lining 5 of a high temperature, low adhesion 10 polymer, such as polytetrafluoroethylene(PTFE). A heating fluid 4' flows in channels 4. The core rod 1 first enters into the core rod receiver 3. This leaves a small gap between core rod 1 and core rod receiver 3 which is made to reflect the coating 15 thickness required for the core rod. Molten polymer is next fed into an entrance port 6 and fills the gap between the core rod 1 and the core rod receiver 3.

The core rod 1 then exits the core rod receiver 3 with a predetermined coating thickness of molten barrier material 6' and enters the conventional injection cavity mold 7 at B. The flow of heating fluid 2' in channel 2 is then interrupted and a cooling fluid 2'' is introduced. The main container molding material 8' is then injected through entry 20 port 8 and flows over the molten barrier material to form a preform with a very thin inner layer comprised 25 of the barrier material 6'.

An alternative to the process described above is to use the core rod receiver 3 at A as a conventional 30 injection mold. In this case, the core rod 1 is first cooled by applying cooling fluid 2'' to channel 2 and the core rod receiver 3 is cooled by cooling fluid, not shown, in the channels 4. The core rod 1 then enters into the core rod receiver 3 and molten barrier 35 material 6' is injected through the entrance port 6, filling the gap between core rod 1 and core rod

- 7 -

receiver 3. The material in the gap solidifies and core rod 1 withdraws from core rod receiver 3 taking the solidified barrier material 6' as an external sleeve since this adheres to core rod 1 rather than to 5 the inner lining 5.

A heating element 9 is next positioned around the core rod 1 as shown by the phantom lines at C to melt the external skin of the barrier material 6' coating sleeve on core rod 1. The heating element 9 then 10 swings out of the way of core rod 1 which then enters injection cavity mold 7 at B and the main molding material 8' is injected through port 8 to produce the finished preform in the manner described.

If the adhesion between the barrier material 6' used in the inner layer of the preform and the main material 8' of the preform require an adhesive or "tie-layer", which materials are conventionally available for many applications, it can be introduced by using another receiver, not shown, identical to the 15 core rod receiver 3 in parallel therewith. The adhesive material is injected into this additional receiver and the core rod 1, after being coated with either a molten layer of barrier material 6' or with a solid layer 8' in a manner already described, is introduced into the additional receiver so as to 20 receive a coat of adhesive prior to entering injection mold cavity 7 shown at B.

Finally, if an interface adhesive is used, the 25 heating of the sleeve formed around the core rod 1 by heater 9 at C can be avoided depending on adhesive and polymers used.

The process thus described can, when desired, be applied to an injection molding machine having a plurality of core rods 1 and cavity molds 7 by 30 providing a core rod receiver 3 with a plurality of cavities and, if necessary, a plurality of core rod 35

- 8 -

receivers for adhesive.

Figure 2 is illustrative of another method for applying a coating 6' to the core rod 1. As shown, a depositor 10 includes an inner channel 11 and a 5 depositing slot 12. Molten barrier material 6' is fed into port 13 where it flows to a depositing slot 12 as shown in Figure 3. The depositor 10 can then be swung into position as shown at A and rotated to apply an even coating of molten barrier material 6' around the 10 core rod 1. The internal channel 2 of core rod 1 is supplied with heating fluid 2' to maintain the coating around core rod 1 in a molten state.

The depositor 10 then swings out of the way as 15 shown at B and the core rod 1 enters the injection cavity mold 7 as shown at C where the main molding material, not shown, is injected to produce a finished preform as before.

The depositing slot 12 (Figure 3) can be 20 adjustable if required to provide an even, controlled layer of deposition on the core rod 1.

If the adhesion between the barrier material 6' used in the inner layer of the preform and the main material 8' of the preform requires an adhesive, not shown, it would be introduced by using a second and 25 identical depositor 10, also not shown. After deposition of the barrier material on the core rod 1, the depositor 10 then swings out of the way and an identical, second depositor, supplied with the adhesive, deposits the adhesive layer prior to the 30 core rod 1 entering the injection molding cavity 7 at C.

This process can be implemented, when desirable, 35 with a multiplicity of core rods 1 and cavity molds 7 by providing a plurality of depositors 10 and, if necessary, a plurality of identical depositors for adhesive.

5 Although not shown, an alternative to coating the core-rod 1 by using a depositor of the type indicated by Fig. 2 is to coat the inside of the preform 14 (Fig. 4) using a depositing device as in Fig. 2 by dimensionally adapted to enter the preform 14 cavity.

10 Considering now Figure 4A, disclosed thereat is a method for applying a thin coating of barrier material 6' directly using a container preform 14. As shown at A, the container preform 14 is inserted into a cooling mantel 20 equipped with cooling channels 21. A radiant heater 15 melts the inner surface of the preform 14 while the main body of the preform 14 is kept cool. At B, the preform 14 is withdrawn from the cooling mantel 20 and a depositor 16 injects an appropriate, accurately metered amount of molten barrier material 6'. At C, a displacement rod 18 having an elongated central channel 19 first enters the preform 14 and displaces the molten barrier material 6' so that it is evenly spread inside the preform 14. If necessary, during this phase, a heating fluid, not shown, can be made to flow in the channel 19.

25 The preform 14 has a slightly tapered inner surface 14' in its topmost area thereby forming a slightly enlarged cavity as shown in Figure 4B which enables the metering tolerance of molten barrier material 6' to be taken up by allowing this to only partially fill the enlarged cavity at 14'. This effect is illustrated at Figure 4C. At position C of Figure 4A, the displacement rod 18 is pressed down hydraulically and can therefore create a very large flow pressure directly in the molten barrier material 6', this being far greater than that which can be generated by conventional injection mold pumping devices. The high pressure thus generated permits even flow of molten barrier material 6' in a very

- 10 -

narrow channel formed between displacement rod 18 and preform 14. This in turn enables a very thin inner layer whereas this would not be possible by conventional injection into such a narrow channel, 5 because the very high pressure needed for inducing flow and filling the whole channel would not be practicable using injection mold pumping devices. Furthermore, since the molten barrier material 6' is premeasured to fill the whole channel formed between 10 the displacement rod 18 and the preform 14, with the exception of the partial filling of the enlarged cavity at 14', a greater control of the evenness of the thin inner layer is possible than that provided by conventional injection molding technology, since such 15 conventional technology cannot meter the amount of material entering the mold.

Finally, when desired, the displacement rod 18 can be rotated at a predetermined speed for enabling better radial flow around the channel formed between 20 displacement rod 18 and preform 14, also contributing to coating evenness. Particularly, since molten polymers are generally thixotropic and reduce their viscosity with applied shear force, the shear force exerted by the rotating displacement rod 18 in the 25 molten barrier material 6' reduces the viscosity and enhances even flow. Additionally, this reduces the hydraulic pressure needed to press the displacement rod 18 into the preform 14. With certain plastics, this shearing action can also enable orientation of 30 the plastic, enhancing its barrier properties, provided the molten barrier material 6' is kept at the appropriate temperature during its displacement.

When the displacement of the molten barrier material 6' is completed, the preform 14 is reinserted 35 into the cooling mantel 20 shown at position A of Figure 4A and a cooling fluid is switched to flow in

place of heating fluid in channel 19. The barrier material 6' now solidifies to form an inner layer 22 within preform 14. If the adhesion of the barrier material 6' of the inner layer 22 with the main material of the preform 14 requires an adhesive or a "tie layer", this can be introduced in the same manner as described before. This results in an adhesive layer, not shown, between the material of the preform 14 and the inner layer 22. Depending on the adhesive system used, the need to melt the internal surface of the preform 14, as represented at A, may prove unnecessary. This process can, as before, be implemented as shown in Figure 2 with a plurality of core rods 1 and cavity molds 7 by providing a plurality of heaters 15, depositors 16, and displacement rods 19. Also, a plurality of blow molding positions can be served by providing a multiplicity of heaters 23 or coolers, if needed, in the same position.

The preform 14 including the barrier layer 22 is now finished and can be passed to a conventional container blowing machine. As shown in Figure 5, a conventional blow molding machine includes radiant heater elements 25 which operate to raise the temperature of the preform 14 above a glass transition temperature, so that the material of the preform 14 can be stretch blown into a blow mold cavity, not shown. Conventional heat shields 24 are also used to protect the screw threads if formed of the opening 26 of the preform 14.

However, in contrast to conventional pre-blow-molding heat treatment, because the layer 22 of the barrier material 6' within the preform 14 is very thin, it can be provided with a differential heat treatment, thus enabling the use of an inner layer 22 with a different glass transition temperature than

- 12 -

5 preform 14. To enable differential heat treatment, a radiant heater 23 is added to the conventional equipment and introduced as shown in Figure 5 to heat the inside of the preform 14 when the inner layer 22 has a higher glass transition temperature than the main material of the preform 14. Alternatively, when 10 the inner layer 22 has a lower transition temperature than the main material of the preform 14, a cooling tube, not shown, is inserted in place of heater 23 to reduce the thermal stress of the thin inner layer 22 within the preform 14.

15 Having thus shown and described what is considered to be the preferred methods and respective embodiments for implementing the subject invention, it should be noted that all modifications, alterations and changes coming within the spirit and scope of the invention are herein meant to be included.

CLAIMS

1. A method of fabricating a relatively thin
2 inner layer of a first polymer within a stretch blown
3 container preform consisting of a second polymer,
4 comprising the steps of:

5 (a) heating a molding core rod;

6 (b) inserting the core rod into a core rod
7 receiver;

8 (c) filling a gap formed between the core rod and
9 the core rod receiver with a first polymer while being
10 in a molten state, said first polymer having a
11 predetermined barrier and/or inertness characteristic
12 so as to form a thin barrier layer on said core rod;

13 (d) removing the core rod from the core rod
14 receiver while the thin barrier layer is still in a
15 molten state;

16 (e) inserting the core rod and the thin barrier
17 layer into an injection cavity mold;

18 (f) cooling the core rod; and

19 (g) feeding a second polymer into the injection
20 mold and flowing said second polymer over the thin
21 barrier layer while still molten, thereby fabricating
22 a preform having a thin inner layer of barrier
23 material.

1. The method of claim 1 and additionally
2 including another step between steps (d) and (e) of
3 forming a layer of adhesive on said thin barrier
4 layer.

1. The method of claim 2 wherein said another
2 step of providing an adhesive layer comprises
3 inserting the core rod with said thin barrier layer
4 formed thereon into a core rod receiver containing
5 adhesive material.

- 14 -

1 4. A method of fabricating a relatively thin
2 inner layer of a first polymer within a stretch blown
3 container preform consisting of a second polymer,
4 comprising the steps of:

5 (a) cooling a molding core rod;
6 (b) cooling a core rod receiver;
7 (c) inserting the core rod into the core rod
8 receiver and forming a gap therebetween;
9 (d) injecting a first polymer in said gap while
10 being in a molten state and having predetermined
11 barrier and/or inertness characteristic so as to form
12 a thin barrier layer of said first polymer on said
13 core rod;
14 (e) removing the core rod from the core rod
15 receiver when the first polymer in the gap solidifies,
16 thereby providing an external sleeve of said first
17 polymer on the core rod;
18 (f) heating the core rod and the external sleeve
19 of said first polymer;
20 (g) inserting the core rod and the external
21 sleeve into an injection cavity mold; and
22 (h) feeding a second polymer into the injection
23 cavity mold and flowing the second polymer over the
24 external sleeve of said first polymer to fabricate a
25 preform having a thin inner layer of barrier material.

1 5. The method of claim 4 and additionally
2 including another step between steps (f) and (g) of
3 forming a layer of adhesive on said sleeve.

1 6. The method of claim 5 wherein said another
2 step of providing an adhesive layer comprises
3 inserting the core rod with said thin barrier layer
4 comprising an external sleeve into a core rod receiver
5 containing adhesive material.

- 15 -

1 7. A method of fabricating a relatively thin
2 inner layer of a first polymer within a stretch blown
3 container preform consisting of a second polymer,
4 comprising the steps of:

- 5 (a) cooling a molding core rod;
- 6 (b) cooling a core rod receiver;
- 7 (c) inserting the core rod into the core rod
8 receiver and forming a gap therebetween;
- 9 (d) injecting a first polymer in said gap while
10 being in a molten state and having predetermined
11 barrier and/or inertness characteristic so as to form
12 a thin barrier layer of said first polymer on said
13 core rod;
- 14 (e) removing the core rod from the core rod
15 receiver when the first polymer in the gap solidifies
16 thereby, providing an external sleeve of said first
17 polymer on the core rod;
- 18 (f) forming a layer of adhesive material on said
19 external sleeve of said first polymer;
- 20 (g) inserting the core rod and the external
21 sleeve into an injection cavity mold; and
- 22 (h) feeding a second polymer into the injection
23 cavity mold and flowing the second polymer over the
24 external sleeve of the first polymer to fabricate a
25 preform having a thin inner layer of barrier material.

1 8. A method of fabricating a relatively thin
2 inner layer of a first polymer within a stretch blown
3 container preform consisting of a second polymer,
4 comprising the steps of:

- 5 (a) heating a molding core rod;
- 6 (b) rotating a coating depositor having a
7 depositing slot therein around the core rod and
8 depositing thereon a thin barrier layer of a first
9 polymer while being in a molten state, said first
10 polymer having predetermined barrier and/or inertness

- 16 -

11 characteristic;

12 (c) removing the depositor from the proximity of
13 the core rod with the thin barrier layer formed
14 thereon;

15 (d) inserting the core rod in an injection cavity
16 mold;

17 (d) cooling the core rod; and

18 (e) feeding a second polymer into the injection
19 mold and flowing the second polymer over the thin
20 layer of said first polymer while still molten to form
21 a preform having a thin inner layer of barrier
22 material.

1 9. The method of claim 8 and additionally
2 including another step between steps (c) and (d) of
3 forming a layer of adhesive on said barrier layer.

1 10. The method of claim 9 wherein said step of
2 forming a layer of adhesive comprises rotating a
3 depositor containing an adhesive around the barrier
4 layer to form an adhesive layer.

1 11. A method of fabricating a relatively thin
2 inner layer of a first polymer within a stretch blown
3 container preform consisting of a second polymer,
4 comprising the steps of:

5 (a) inserting a container preform of said second
6 polymer into a cooling mantle;

7 (b) inserting a radiant heating element inside of
8 the preform for melting the inner surface of the
9 preform while keeping the main body of the preform
10 relatively cool;

11 (c) withdrawing the preform from the cooling
12 mantle;

13 (d) placing a depositor of first polymer adjacent
14 to the preform and injecting a predetermined amount of

15 first polymer while in a molten state, and having
16 predetermined barrier and/or inertness characteristics
17 into the preform;

18 (e) inserting means into the preform for
19 displacing the molten first polymer and evenly
20 spreading the first polymer inside the preform to form
21 an inner layer therein; and

22 (f) reinserting the preform into the cooling
23 mantle and cooling the spreaded first polymer until it
24 solidifies and forms an inner layer within the
25 preform.

1 12. A method as defined by claim 11 and
2 additionally including the step of heating the means
3 for displacing to enhance the spreading of the first
4 polymer inside the preform following step (e).

1 13. The method of claim 11 and additionally
2 including another step between steps (c) and (d) of
3 forming a layer of adhesive on the inside of said
4 preform.

1 14. The method of claim 11 and additionally
2 including the step of cooling the means for displacing
3 for reducing the thermal stress of said inner layer.

1 15. The method of claim 11 and additionally
2 including another step following step (3) of rotating
3 said means for displacing and evenly spreading the
4 first polymer.

1 16. The method of claim 11 and additionally
2 including a step (g) of inserting heating means in the
3 preform for reheating the inner layer to facilitate a
4 subsequent blow molding of the inner layer.

1 17. The method of claim 11 and additionally
2 including a step (g) of inserting cooling means in the
3 preform for further cooling the inner layer to reduce
4 thermal stress in the inner layer.

1 18. A system of fabricating a relatively thin
2 inner layer of a first polymer within a stretch blown
3 container preform consisting of a second polymer,
4 comprising:

- 5 (a) molding core rod and a core rod receiver;
- 6 (b) means for heating the molding core rod and
7 for inserting the core rod into the core rod receiver;
- 8 (c) means for filling a gap formed between the
9 core rod and the core rod receiver with a first
10 polymer while being in a molten state, said first
11 polymer having a predetermined barrier and/or
12 inertness characteristic so as to form a thin barrier
13 layer on said core rod;
- 14 (d) means for removing the core rod from the
15 core rod receiver while the thin barrier layer is
16 still in a molten state;
- 17 (e) an injection cavity mold;
- 18 (f) means for inserting the core rod and the thin
19 barrier layer into the injection cavity mold and
20 cooling the core rod; and
- 21 (g) means for feeding a second polymer into the
22 injection mold and flowing said second polymer over
23 the thin barrier layer while still molten, thereby
24 fabricating a preform having a thin inner layer of
25 barrier material.

1 19. The system of claim 18 and additionally
2 including means for forming a layer of adhesive on
3 said thin barrier layer prior to flowing said second
4 polymer over the barrier layer.

1 20. A system of fabricating a relatively thin
2 inner layer of a first polymer within a stretch blown
3 container preform consisting of a second polymer,
4 comprising:

- 5 (a) a molding core rod and a core rod receiver;
- 6 (b) means for cooling the core rod receiver;
- 7 (c) means for inserting the core rod into the
8 core rod receiver and forming a gap therebetween;
- 9 (d) means for injecting a first polymer in said
10 gap while being in a molten state and having
11 predetermined barrier and/or inertness characteristic
12 so as to form a thin barrier layer of said first
13 polymer on said core rod and thereafter removing the
14 core rod from the core rod receiver when the first
15 polymer in the gap solidifies, providing thereby an
16 external sleeve of said first polymer on the core rod;
- 17 (e) means for heating the core rod and the
18 external sleeve of said first polymer;
- 19 (f) an injection cavity mold;
- 20 (g) means for inserting the core rod and the
21 external sleeve into the injection cavity mold; and
- 22 (h) means for feeding a second polymer into the
23 injection cavity mold and flowing the second polymer
24 over the external sleeve of said first polymer to
25 fabricate a preform having a thin inner layer of
26 barrier material.

1 21. The system of claim 20 and additionally
2 including means for forming a layer of adhesive on
3 said sleeve.

1 22. A system of fabricating a relatively thin
2 inner layer of a first polymer within a stretch blown
3 container preform consisting of a second polymer:

- 4 (a) a molding core rod and a core rod receiver;
- 5 (b) means for cooling the molding core rod and

- 20 -

6 the core rod receiver;

7 (c) means for inserting the core rod into the
8 core rod receiver and forming a gap therebetween;

9 (d) means for injecting a first polymer in said
10 gap while being in a molten state and having
11 predetermined barrier and/or inertness characteristic
12 so as to form a thin barrier layer of said first
13 polymer on said core rod;

14 (e) means for removing the core rod from the
15 core rod receiver when the first polymer in the gap
16 solidifies thereby, providing an external sleeve of
17 said first polymer on the core rod;

18 (f) means for forming a layer of adhesive
19 material on said external sleeve of said first
20 polymer;

21 (g) an injection cavity mold;

22 (h) means for inserting the core rod and the
23 external sleeve into the injection cavity mold; and

24 (i) means for feeding a second polymer into the
25 injection cavity mold and flowing the second polymer
26 over the external sleeve of the first polymer to
27 fabricate a preform having a thin inner layer of
28 barrier material.

1 23. A system of fabricating a relatively thin
2 inner layer of a first polymer within a stretch blown
3 container preform consisting of a second polymer:

4 (a) a molding core rod;

5 (b) means for heating the molding core rod;

6 (c) a coating depositor having a depositing slot
7 therein locatable around the core rod and including
8 means for depositing a thin barrier layer of a first
9 polymer being in a molten state on said core rod, said
10 first polymer having predetermined barrier and/or
11 inertness characteristic;

12 (d) means for removing the depositor from the

13 proximity of the core rod after the thin barrier layer
14 is formed thereon;

15 (e) an injection cavity mold;

16 (f) means for inserting the core rod in the
17 injection cavity mold;

18 (g) means for cooling the core rod; and

19 (h) means for feeding a second polymer into the
20 injection mold and flowing the second polymer over the
21 thin layer of said first polymer while still molten to
22 form a preform having a thin inner layer of barrier
23 material.

1 24. The system of claim 23 and additionally
2 including means for forming a layer of adhesive on
3 said barrier layer.

1 25. A system of fabricating a relatively thin
2 inner layer of a first polymer within a stretch blown
3 container preform consisting of a second polymer:

4 (a) a container preform;

5 (b) a cooling mantle;

6 (c) means for inserting the container preform of
7 said second polymer into the cooling mantle;

8 (d) a radiant heating element insertable inside
9 of the preform for melting the inner surface of the
10 preform while keeping the main body of the preform
11 relatively cool;

12 (e) means for withdrawing the preform from the
13 cooling mantle;

14 (f) a depositor of a first polymer positionable
15 adjacent the preform for injecting a predetermined
16 amount of said polymer in a molten state into the
17 preform, said first polymer having predetermined
18 barrier and/or inertness characteristics;

19 (g) means insertable into the preform for
20 displacing the molten first polymer and evenly

- 22 -

21 spreading the first polymer inside the preform to form
22 an inner layer therein; and

23 (h) means for again inserting the preform into
24 the cooling mantle and cooling the spreaded first
25 polymer until it solidifies, thereby forming an inner
26 barrier layer within the preform.

1 26. The system of claim 25 and additionally
2 including means for heating the displacing means to
3 enhance the spreading of the first polymer inside the
4 preform.

1 27. The system of claim 25 and additionally
2 including means for forming a layer of adhesive on the
3 inside of said preform prior to receiving said first
4 polymer.

1 28. The system of claim 25 and additionally
2 including means for cooling the displacing means for
3 reducing the thermal stress of said inner layer.

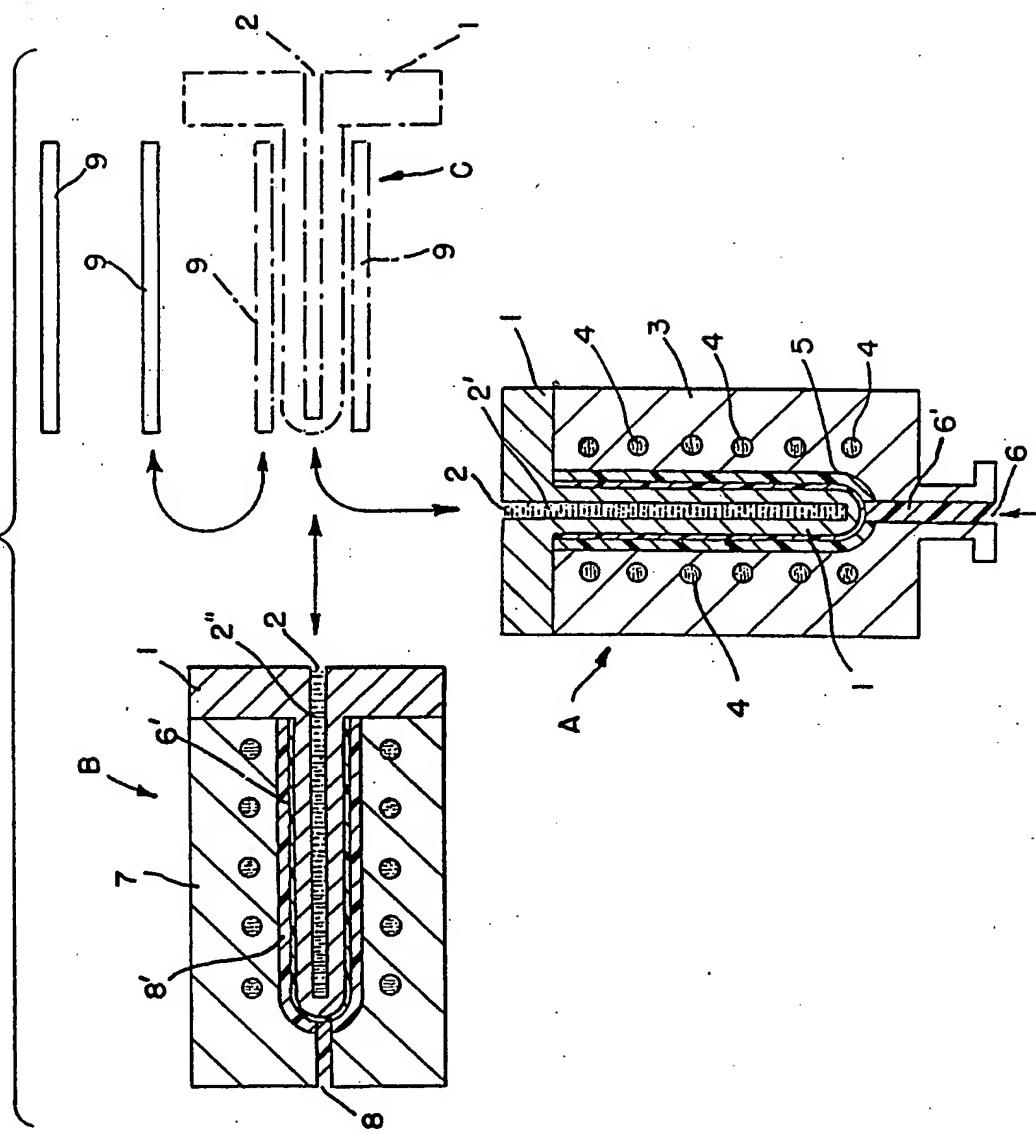
1 29. The system of claim 25 and additionally
2 including means for rotating said means for displacing
3 and evenly spreading the first polymer.

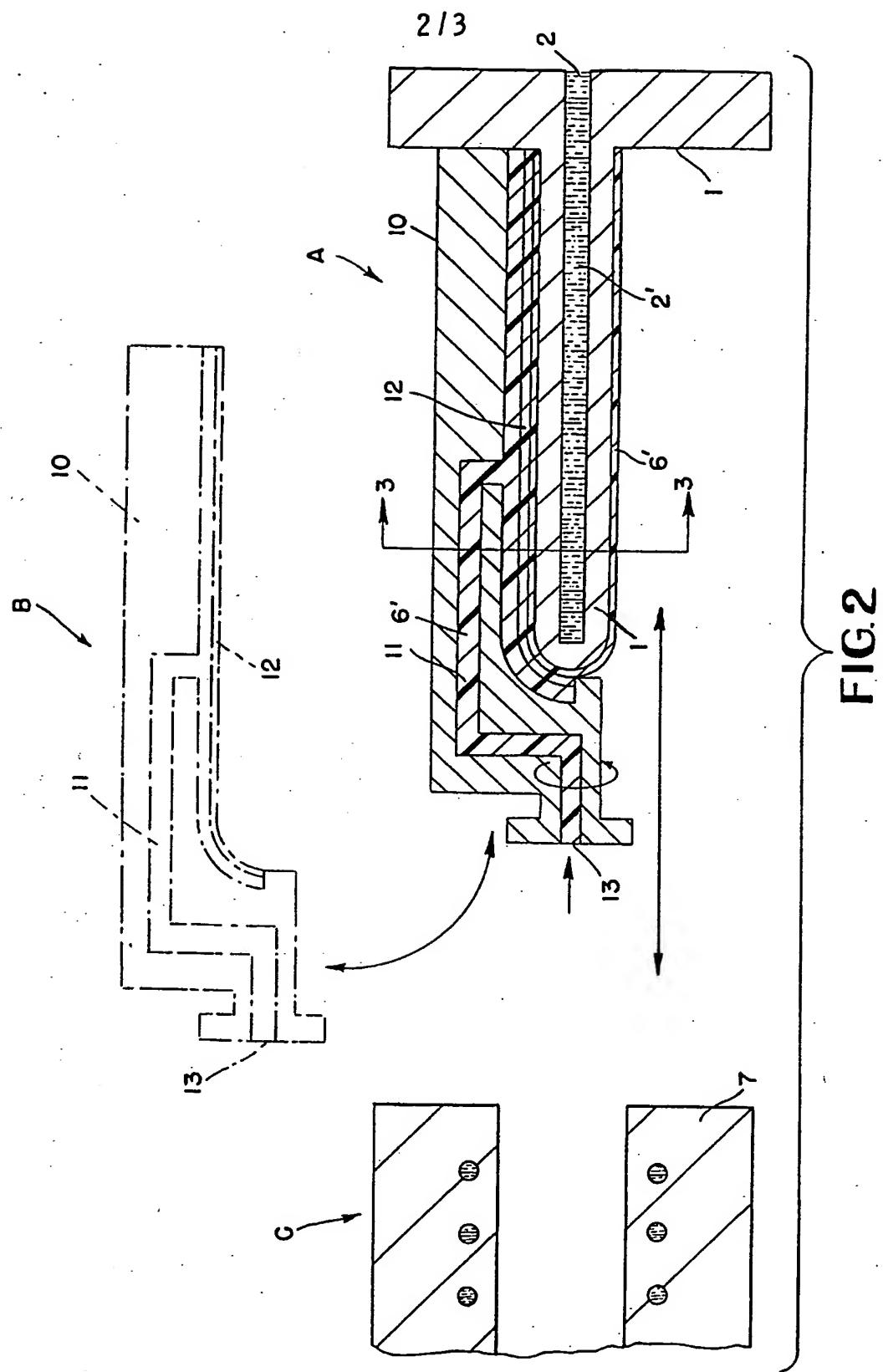
1 30. The system of claim 25 and additionally
2 including means for reheating the inner layer within
3 the preform to facilitate a subsequent blow molding of
4 the inner layer.

1 31. The system of claim 25 and additionally
2 including means for further cooling the inner layer in
3 the preform to reduce the thermal stress therein when
4 the inner layer has a lower transition temperature
5 than that of the preform.

113

EIGI





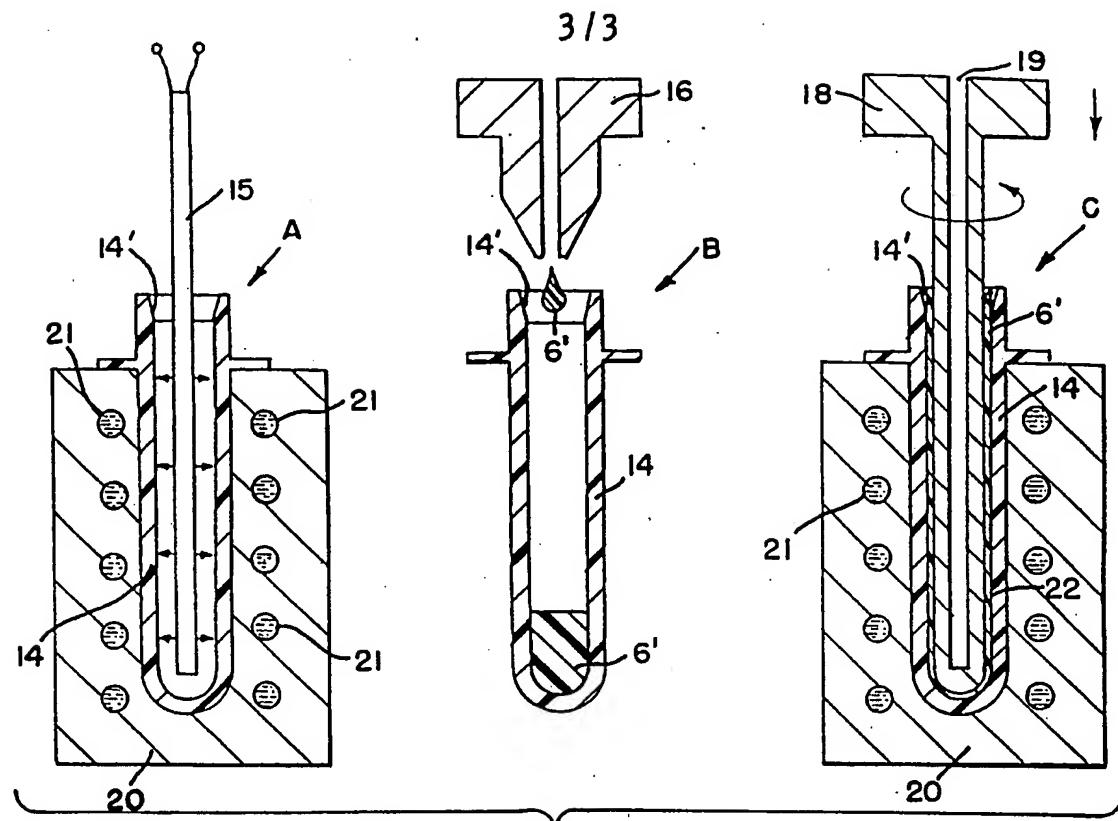


FIG. 4A

FIG. 4B

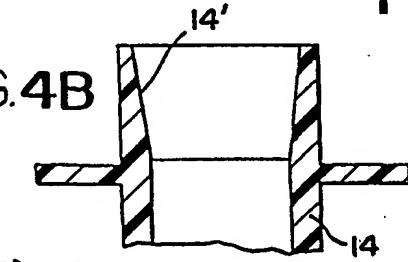


FIG. 4C

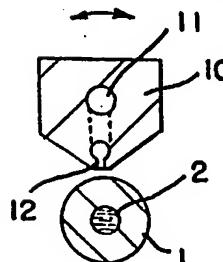
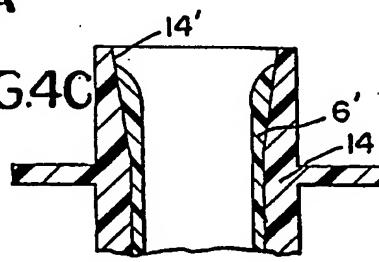


FIG. 3

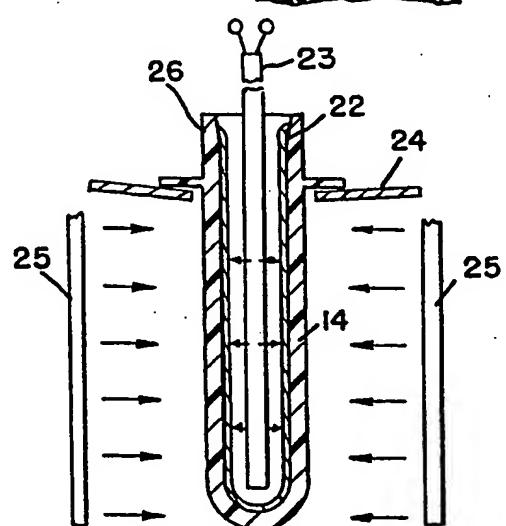


FIG. 5

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 95/01646

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B29C45/16 B29C49/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B29C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB,A,2 138 350 (TOYO SEIKAN KAISHA) 24 October 1984	1-7, 18-22
A	see the whole document	8,23
X	GB,A,1 482 956 (ILIKON CORP.) 17 August 1977	1,4,18, 20
Y	see the whole document	2,5,7, 19,21,22
X	GB,A,2 117 698 (KATASHI AOKI) 19 October 1983	1,4,18, 20
	see the whole document	
X	US,A,3 947 176 (RAINVILLE) 30 March 1976	1,4,18, 20
	see the whole document	
		-/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- *&* document member of the same patent family

1

Date of the actual completion of the international search

1 June 1995

Date of mailing of the international search report

27 / 05 / 95

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentiaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+ 31-70) 340-3016

Authorized officer

Bollen, J

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 95/01646

C(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 11 no. 6 (M-551) [2453] ,8 January 1987 & JP,A,61 185417 (MITSUBISHI PLASTICS) 19 August 1986, see abstract ---	1,4,18, 20
X	PATENT ABSTRACTS OF JAPAN vol. 10 no. 51 (M-457) [2108] ,28 February 1986 & JP,A,60 201909 (TOYOU SEIKAN) 12 October 1985, see abstract ---	1,4,18, 20
Y	AU,D,2 693 871 (IMPERIAL CHEMICAL INDUSTRIES) 28 September 1972 see claims 1,3 ---	2,5,7, 19,21,22
A	PATENT ABSTRACTS OF JAPAN vol. 8 no. 180 (M-318) [1617] ,18 August 1984 & JP,A,59 071832 (TOYOU SEIKAN) 23 April 1984, see abstract ---	11,25
A	FR,A,2 314 042 (CURETTI) 7 January 1977 see claims 1,3; figures 1-6 ---	11,25
A	DE,A,20 41 514 (HESSER MASCHINENFABRIK AG) 24 February 1972 see the whole document -----	11,25

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 95/01646

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
GB-A-2138350	24-10-84	JP-C- 1483731		27-02-89
		JP-A- 59158232		07-09-84
		JP-B- 63030132		16-06-88
		SE-B- 463755		21-01-91
		SE-A- 8401063		29-08-84
		US-A- 4517274		14-05-85
		US-A- 4534930		13-08-85
GB-A-1482956	17-08-77	NONE		
GB-A-2117698	19-10-83	JP-A- 58168531		04-10-83
		DE-A- 3311608		06-10-83
		FR-A,B 2524373		07-10-83
US-A-3947176	30-03-76	NONE		
AU-D-2693871	28-09-72	NONE		
FR-A-2314042	07-01-77	CH-A- 595969		28-02-78
		AT-B- 364761		10-11-81
		CA-A- 1077217		13-05-80
		DE-A- 2626342		23-12-76
		GB-A- 1555381		07-11-79
		JP-C- 1316995		15-05-86
		JP-A- 51151773		27-12-76
		JP-B- 60047086		19-10-85
		US-A- 4324541		13-04-82
		US-A- 4243620		06-01-81
DE-A-2041514	24-02-72	NONE		